Flexible Thermoelectric Power Generators Based on Electrochemical Deposition

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論文内容要約

Body area network (BAN) is a promising technology for many applications in the residential and medical fields. However, most of the wearable electronics devices based on this technology are still powered by batteries that need to be recharged and replaced frequently. For these wearable devices, it is necessary to have a power recharging mechanism without a user's interference. One possible solution for powering wearable devices without a battery is to harvest the thermal energy from human body temperature. The development of thermoelectric power generators (TEGs) has merited much attention due to its capability to convert low-grade waste heat into electrical energy using the Seebeck effect. However, human body are not flat but deformable, thus it indicates an essential need of flexible thermoelectric power generators **(**FTEGs) for the thermoelectric conversion applications. When a FTEG is attached onto the skin, the heat from the human body flows through the device. The voltage would be created in a FTEG due to the temperature difference between the skin and the ambient environment.

Electrochemical deposition is one of potential methods to synthesize thick films of thermoelectric materials with high quality morphology, compactness, thickness and thermoelectric properties. Using the electrochemically deposited materials for the applications of flexible micro devices has a great promise for thermal energy harvesters. However, due to the substantial obstacle of integrating the materials into flexible microsystem platform with controllable architectures, the application of electrochemical deposition is very limited to date. Therefore, this thesis mainly focuses on addressing the associated challenges by fabricating flexible thermoelectric power generators using electrochemical deposition method.

To fabricate and optimize the performance of FTEGs, there are many issues need to be solved. Because the temperature difference depends on the thickness of the thermocouples (TCs), using thicker thermocouples, the more heat energy can be harvested. However, the synthesis of thick thermoelectric materials in micro devices remains a challenge. In previous works, thermoelectric thin films of Bi_2Te_3 and Sb_2Te_3 have been deposited on solid or flexible substrates. In these studies, the thermoelectric energy conversion performances as an energy harvester are low due to the high internal electrical resistance of the thin film of thermoelectric elements. To enhance the working performances, thick films of thermoelectric materials are necessary. To achieve thick films of thermoelectric materials and improve the working performances, screen-printing, inkjet printing, molding, and vacuum deposition are the recently common methods. According to the previous works, all of best devices have been based on methods that allow synthesizing the thermocouples with the thickness of several hundred micrometers. Although the electrochemical deposition can synthesize thick films of thermoelectric materials, this method has not been effectively used for the applications on the flexible thermoelectric power generators so far. All of previous works based on the electrochemical deposition only aim to fabricate solid TEGs (STEGs). In this thesis, thick films of thermoelectric materials (Bi_2Te_3 and Sb_2Te_3) have been synthesized using electrochemical deposition for the fabrication of FTEGs. Moreover, enhancing the figure of merit *ZT* values of thermoelectric materials is also a difficult objective. So far, the figure of merit *ZT* values of thermoelectric materials at room temperature synthesized using electrochemical deposition are usually lower than other materials working at high temperatures.

Another obstacle that needs to be solved is the fabrication process. Because thermoelectric materials are electrochemically deposited on a solid silicon substrate. To fabricate a flexible device, a new fabrication process based on MEMS technology needs to be developed to integrate thermoelectric materials with a flexible support. Many previous works have reported that STEGs with electroplated materials can be completed by a two-substrate method. Herein, N-type and P-type thermoelectric materials are deposited separately on two different substrates. A single substrate with an individual material would be joined with each other at the end of the process. Another approach for STEGs fabrication is to deposit both N-type and P-type thermoelectric materials on the same substrate. The advantage of this method is that electrical contacts can be grown by the electroplating deposition or boding materials. However, this method encounters another problem. Since TCs are deposited on a metal seed layer, an electrical short-circuiting behavior in the TCs is caused if the seed layer is not removed. The laser cutting method has solved this behavior. Nevertheless, these methods can be only applied to solid membrane substrates. Hence, the fabrication of FTEGs based on sputtered or evaporated thermoelectric materials upon a flexible substrate is still a widely used method. That is the reason why all the best FTPGs to date are based on a print-screening method, which shows the possibility to synthesize thick thermoelectric films. However, the print-screening method has the disadvantage of the low integration of TCs.

Structures of the device can improve the temperature harvesting performance. Therefore, many structures of FTEGs have to be discussed. All structures are simulated using the finite element method. Meanwhile, the actual devices are fabricated and compared to prove the validity of the idea. The thermal harvesting capability has been evaluated along with internal electrical resistances, open-circuit voltages, and generated power densities near room temperature under a free convection condition.

By solving afore-mentioned challenges, this research aims at developing flexible thermoelectric power generators for thermal energy harvesting applications from many approaches as follows:

The possibility of a deposition of thick and stable thermoelectric films using electrochemical deposition method has been demonstrated in chapter 2. The electrolytes are used with a low concentration of cations and ions, resulting in a controlled low deposition rate. Therefore, the amorphous material is easily crystallized during the pulsed deposition. By this method, without the necessity of using non-aqueous additives and a soluble anode, highly oriented Bi_2Te_3 and Sb_2Te_3 thick films with a bulk-like structure are successfully synthesized with high Seebeck coefficients and low electrical resistivities. Several hundred-micrometers-thick Bi_2Te_3 and Sb_2Te_3 films are obtained. The Seebeck coefficients for the Bi_2Te_3 and Sb_2Te_3 films are −150 ± 20 and 170 ± 20 μV/K, respectively. Additionally, the electrical resistivity for the Bi_2Te_3 is 15 ± 5 μΩ·m and is 25 ± 5 μΩ·m for the Sb_2Te_3. Both of Bi_2Te_3 and Sb_2Te_3 exhibit low conductivities of approximately 1.4 ± 0.1 W/m·K and 1.5 ± 0.1 W/m·K, respectively. As a result, the figure of merit ZT values of Bi_2Te_3 and Sb_2Te_3 are 0.32 and 0.24, respectively.

An idea of improving thermoelectric properties by inclusions of nanoparticle in composite materials approached by the electrochemical co-deposition is demonstrated in chapter 3. The 5 nm-diameter gold particles are embedded in the nanostructure of Bi_2Te_3. As a result, the Seebeck coefficient is achieved as much as 2.5 times larger than the best result obtained in chapter 2 (~ -400 μV/K) while the electrical resistivity increases by the factor of seven (~140 μΩ·m). Additionally, the thermal conductivity of Bi_2Te_3 composite is approximately three times smaller than that of Bi_2Te_3 (~0.5 W/m·K and 1.4 W/m·K, respectively). Finally, the figure of merit *ZT* of composite material is approximately 0.62, which is two times larger than that of Bi_2Te_3 (~0.3). The gold nano-particles bismuth telluride shows the best values of Seebeck coefficient, thermal conductivity and figure of merit *ZT* among the bismuth telluride synthesized using the electrochemical deposition to date.

A new fabrication of flexible thermoelectric power generators approached from the electrochemical deposition method and MEMS technologies is introduced in chapter 4 and chapter 5. A new fabrication technique based on MEMS technology, using a silicon substrate as a sacrificial substrate is proposed and performed to realize self-supporting flexible micro-devices. With the proposed process, π-type and Y-type FTEGs have been successfully fabricated. Two π-type generators with different material combinations (Bi_2Te_3-Cu and Bi_2Te_3-Sb_2Te_3) are fabricated and compared in chapter 4. The devices are fabricated with the π-type structure embedded in a flexible material, where the top and bottom supporting substrates are eliminated. The thickness of Bi_2Te_3 and Sb_2Te_3 thermocouples is 200 μm. The usage of the thick thermoelectric films is especially advantageous for devices operating at small-to-moderate temperature differences, such as the human body temperature. From the human body temperature (~37ºC) and environment ambience (15°C), the Bi_2Te_3-Cu and Bi_2Te_3-Sb_2Te_3 based devices can harvest approximately from 2 ˜ 4ºC temperature difference and generate high output power densities from 1 μW/ cm^2 and 4 μW/cm^2, respectively.

An idea of lateral Y-type TE cells instead of conventional vertical π-type cells is proposed to enhance the performance of harvesting the temperature in chapter 5. The advantages of the novel Y-type structure have been proved to optimize the device performance significantly. Basically, the structure consists of N type-bismuth telluride and P type-antimony telluride, which are deposited laterally on the membrane. The Y-type structure of TCs sandwiched between two thick polymer layers with low thermal conductivity can reduce the heat loss in the vertical direction. Heat is guided to the TCs via copper thermal guides, which are designed to lead the heat flux vertically from bottom to top sides of the device. A new fabrication process is also proposed for the Y-type structure. The larger temperature difference is obtained due to the longer-distance heat transfer of Y structure. With the temperature difference between the human body (approximately 37°C) and environment ambience (15°C), fabricated devices can harvest approximately 6ºC. The output power of the device is approximately 3 μW/cm^2.

In summary, this thesis has successfully fabricated FTEGs using the electrochemical deposition. The highly scalable and new devices demonstrated in this work open up opportunities for the applications of electrochemically deposited thermoelectric materials**.**